Polymeric Biomaterials with Complimentary Role in Joint Endoprosthesis

II. Compositional and morpho-structural analysis

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Successfully used in bone surgery for more than 65 years, self-hardening organic cements (CCOs), in particular acrylic cements, are today, the most advanced complementary biomaterials used in articular endoprosthesis. One of the strategies for obtaining of performing anchorage of artificial implants is to develop new acrylic cements with improved physical, chemical and biomechanical characteristics. The aim of this paper was to identify the compositional and morpho-structural changes of acrylic cements induced by the composition of the liquid phase of the material. Such changes influence the potential to generate the physical bonds responsible for fixation and stabilization of endoprosthesis. The samples studied had different compositions due to the mixture of acrylic monomers, methyl methacrylate (MMA) and butyl acrylate (BuA) in the liquid component of cement. The MMA / BuA ratio varied between 1/0 v / v and 1/4 v / v. Changes in the composition and morphology of cement samples have been highlighted by ESCA (Electron Spectroscopy for Chemical Analysis), EDX (Energy-Dispersive X-ray Spectroscopy), IR spectroscopy and SEM images. The obtained data show that minor changes in cement composition can significantly influence morpho-structural characteristics such as pore size and their distribution in the mass of fixing material.

Keywords: Organic bone cements, ESCA compositional analysis, EDX elemental analysis, scanning electron microscopy

Used for more than 65 years in total hip arthroplasty, self-hardening organic cements (CCO) have applications in the surgical treatment of fractures or bone tumors and transcutaneous vertebroplasty [1-3].

The successful use of acrylic cements as fixation materials for orthopedic endoprosthesis implies a detailed knowing of various properties and applications of these biomaterials [4-7].

Unlike metallic devices (screws, plates, rods) that are used in orthopedic surgery, organic cements used as fixation materials for endoprosthesis are less invasive and less likely to deteriorate the surrounding tissues. Furthermore, the close adhesion between cement and bone and between cement and prosthesis lead to an optimum distribution of the tension and strain energy at the interface.

The fixation of an implant by cementation is based on forming a stable interface between the prosthesis and the cement, a mechanical adhesion of the cement on bone and obtaining a homogenous and cohesive layer of cement. Thus, a biomaterial used for fixation/consolidation of a prosthesis has to have a high affinity for the surrounding environment (metal, bone), as well as an adequate cohesion in order to sustain the mechanical solicitation during the use of the prosthesis.

The requirement for a successful long term prosthesis is a stable bond between the prosthesis and the adjacent tissue [8]. This bond is weakened in time due to severe biological conditions, high and continuous surface tension on the joint, which, in time, can lead to clinical complications such as periprotetic fracture, loosening and periprotetic osteolysis [9].

The aim of this study is to evaluate the compositional and morpho-structural modifications of some organic cements due to the modification of their nature and the ratio between the solid and liquid components of the cement.

Experimental part

Materials and methods

i)Cement preparation

We have prepared three series of cements (CC, CP, CS) with a solid component of commercial materials and a liquid component containing two acrylic monomers in different ratios.

In all the samples, the polymeric powder of the commercial materials was used without modifying the composition. The compositional characteristics of the solid phase of the cements are shown in table 1, as indicated by the producer [10].

The liquid phase of the material was prepared with methyl methacrylate (MMA) and butyl acrylate (BuA), from Merck. The monomers have been purified by common methods and have been kept in the same conditions as the solid phase of the commercial materials until the preparation of the cements (an addition of 75 ppm of hydroquinone, in closed dark flasks, maximum temperature of 20°C).

Even though the ratio between the solid and liquid components was kept constant (2/1 g/mL), the samples in the same series had different composition due to the mixture of acrylic monomers. The ratio MMA/BuA varied between 1/0 v/v and 1/4 v/v.

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Cement samples	Solid phase composition	Cement type/ Manufacturer company
CC Series	PMMA - 85 % $BaSO_4$ - 12 % POB - 3 %	Cemex XL / Tecres Medical Advancing High Technology S.p.A., Verona, Italy [10a].
CP Series	P(MMA-co-S) - 21,1% PMMA - 67,05 % $BaSO_4$ - 10 % POB - 1,85 %	Endurance / Depuy International Ltd., Blackpool, UK [10b].
CS Series	P(MMA-co-S) - 75 % PMMA - 15 % $BaSO_4$ - 8,3 % POB - 1,7 %	Surgical SimplexP / Howmedica International Ltd., London, UK [10c].

Table 1
COMPOSITION OF THE SOLID COMPONENT USED IN THE PREPARATION OF THE CEMENT SAMPLES

The cements were prepared manually, using the experimental protocol mentioned earlier (in another paper) [11,12]. The samples were placed on non-absorbable and non-porous supports (glass, metal) until the hardening of the material.

ii)Compositional analysis

The qualitative and quantitative compositional analysis was done using a scanning electron microscope type Quanta 200, equipped with an Energy Dispersive X-ray module (EDX).

iii)Electronic microscopy

The cement samples were investigated with a scanning electron microscope type Quanta 200, working at 15 kV with secondary electrons. The samples were placed on aluminum stubs and examined in the ESEM mode.

Results and discussions

The fixation and stabilization of the prosthesis is a result of an assemble of chemical and physical processes of high complexity that occur from the moment of application of the cement until it's hardening.

The hardening of the cement (the grip) occurs due to the polymerization of the monomers in the liquid component into the polymeric matrix of the solid component. The hardening mechanism, the kinetics of the process, the microstructural growth, the relationship between microstructure and macroscopic properties of the cements can be considerably modified when the nature and/or the component's concentration are modified: monomers, polymeric matrix.

The modifications in the cement's forming are highlighted through the differences shown by ESCA compositional analysis, IR spectroscopy and scanning electron microscopy.

The different composition of the prepared cements can be seen from the data obtained with EDX elemental analysis.

The EDX spectra presented in figure 1 allow the evaluation of compositional variations that occur due to the partial replacement of MMA with BuA.

The obtained data suggests a variation of 2-3% of the carbon and oxygen content in the cements (table 2).

Although the compositional modifications may seem to have small shifts in values, they can produce significant modifications over the properties of the cements. These modifications can influence the potential of generating physical bounds that are responsible with the fixation and stabilization of the prosthesis. This potential is influenced by the molecular and supramolecular structure of the macromolecules in the acrylic cements. The possibility of forming physical bounds indicates the compatibility of the cements with the support material (bone tissue or prosthesis).

During the cementing process, Van der Waals secondary bounds and hydrogen bounds are the ones responsible for the adhesion cement-support, which is specific to polar

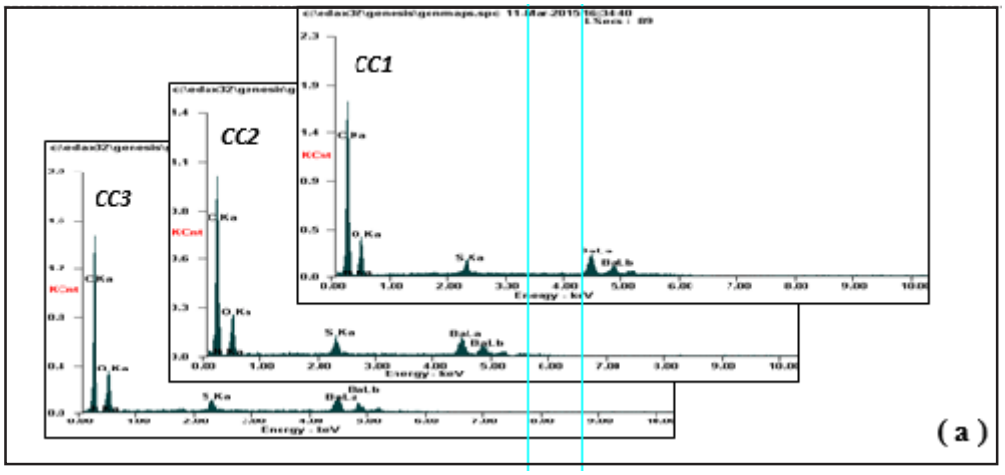

Fig. 1. EDX spectra of acrylic cements: (a) CC series

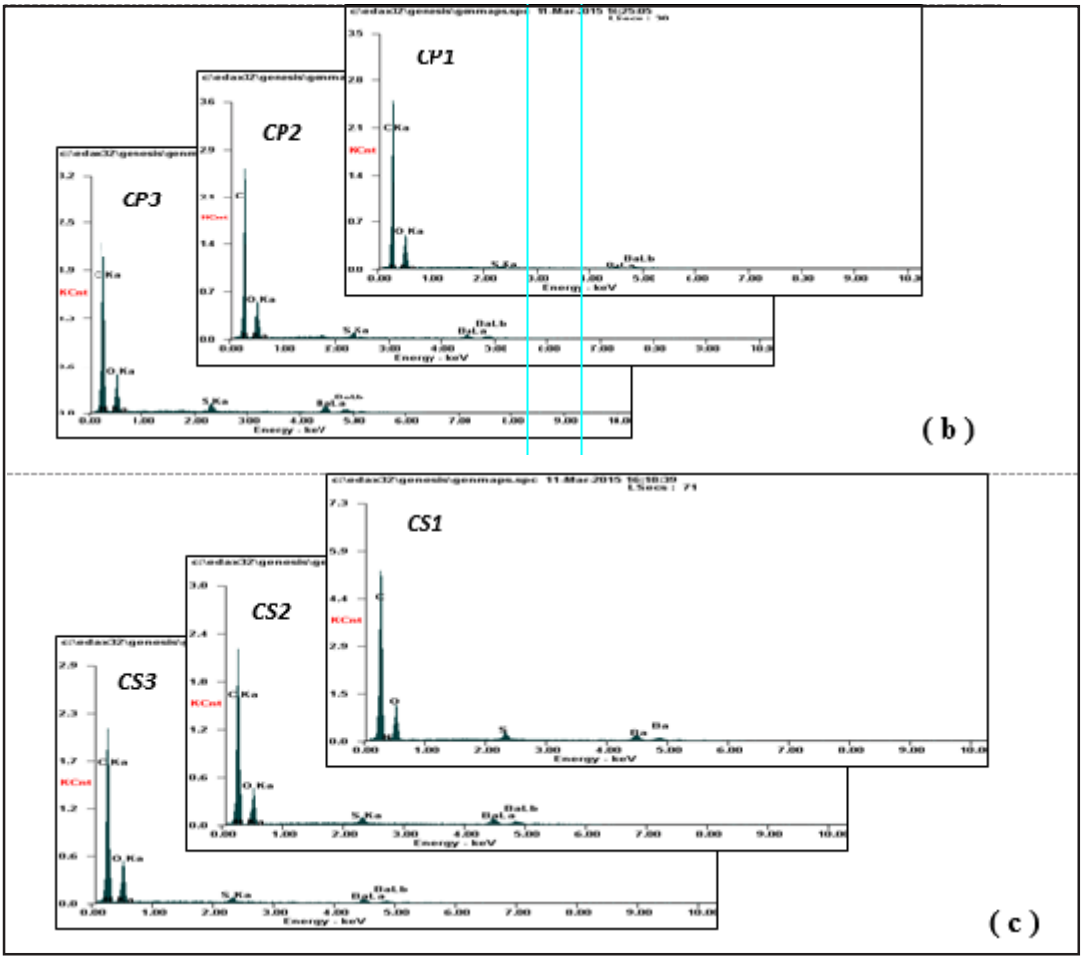

Fig. 1. EDX spectra of acrylic cements: (b) CP series, (c) CS series

Element	Wt (%)								
	CC1	CC2	CC3	CP1	CP2	CP3	CS1	CS2	CS3
CK	66.78	67.42	68.19	73.69	71.86	69.72	72.16	72.72	70.67
OK	16.82	18.82	19.08	22.57	22.56	22.15	21.66	19.95	23.52
NK	00.00	00.00	00.38	00.00	00.58	01.52	00.31	00.00	01.11
SK	01.78	01.93	01.56	00.61	00.78	01.09	01.06	01.06	00.78
BaL	14.63	11.84	10.78	03.13	04.22	05.52	04.82	06.26	03.92

Table 2
COMPOSITION OF ACRYLIC CEMENTS SHOWN BY EDX SPECTRA

substances such as acrylic resins. Since the force of the secondary bounds decreases with the increase in distance of merely a couple of Å, the number and the accessibility of the polar groups determine the capability of adhesive bounds occurring at the interface cement-bone tissue and cement-prosthesis.

It is thus expected that the materials with a higher number of polar groups (BuA units) and more flexible chains to present a higher adhesive potential.

On the long term, the quality and stability of the cements is affected by the incorporation of air in the cement's pores, which can diminish the cement's strength up to the point of a failure in the joint reconstruction. Moreover, a high porosity increases the negative effect of the adsorbed substances at the interface cement-bone.

The pores in the periprosthetic shell can occur during the blending of the components, as well as due to evaporation of the monomers during the polymerization process in the presence of high temperature. Furthermore, the air can be trapped in cement during blending, transfer or application of the material [13].

A high porosity in the cement is responsible for creating and spreading cracks. In porous materials, the crack occurs as a result of gradual cleavagesin the material's mass. James et al. have shown that if the strain exceeds strain resistance, the cracks start from the interior pores and extend towards the surface [14]. Likewise, bigger pores are more susceptible to initiate cracks (fractures) compared to the internal micro-pores. Thus being said, in order to improve the strain resistance, the decrease of inner pores in the cements may be a solution. For an efficient fixation of the prosthesis, the total porosity of the cement has to be $\phi < 5\%$ [15]. One of the most important methods for preventing pore formation is blending the components under vacuum conditions, as well as preparing the cement through centrifugation of the polymer/monomer blend.

Interfacial porosity is a phenomenon that has been studied fairly recently compared to the internal porosity of the cement. The appearance of pores at the interface is not significantly influenced by the blending process of the components, surface treatments of the medullary canal or by the alloy, design and porosity of the prosthesis'

surface. Arthroscopic observations of the cement-implant interface suggest that the interfacial porosity is not due to the chemical or thermal characteristics of the cement-prosthesis system, but a consequence of the rheological process of inserting the implant [16].

The images obtained for these samples offer data regarding the porosity of the material, more precisely the distribution and size of the pores.

Macroporous structures (pores bigger than 1 mm in diameter) can be highlighted radiologically, but for the micro- and nano-metric characterization of the material's surface or its internal morphology the use of scanning electron microscopy (SEM) is needed. This is a useful and adequate method to analyze the surface of materials with medical applications, giving information about the morphology and topography of the sample. Furthermore, SEM micrographs give information about the shape, size and structure of the polymer pearls included in the cement's solid component, as well as the placement of the opacifying agent ($BaSO_4$) in the matrix of the acrylic component [17,18].

The SEM micrographs show that the samples CC2 and CC3 have a porosity higher than the reference material CC1 (fig. 2).

It can be seen that the sample with lower content of BuA has a high number of small pores, and that in the CC3 sample, which has a higher content of BuA, the pores are larger. The modification of the composition is reflected by the internal porosity, as well as the placement of the opacifying agent. The BaSO4 particles tend to agglomerate and are deposited onto the polymer pearls formed during the hardening of the cement (fig. 2).

SEM micrographs of the samples with low content of BuA (CP series) show that the reference sample CP1 has a rather smooth surface, with minimal porosity and uneven deposits of $BaSO_4$ (fig. 3-a). The sample CP2 has un uneven porosity, with pores of various sizes, and an increase in the deposits of radio-opaque additives on the surface of the polymer micro-pearls (fig. 3-b). The sample CP3 shows a high porosity, with pores of similar sizes, with an even distribution all over the surface, as well as a rather even coverage with particles of $BaSO_4$ of around 1 µm (fig. 3-c).

The structure of the samples with higher concentration of substitute monomer is different from the samples that do not contain, or have a low content of BuA. Thus, SEM micrographs of the CS1 sample show a high porosity, with round pores of up to 50 µm and inorganic material ($BaSO_4$) at their edges (fig. 4-a).

The CS2 sample has a decrease in porosity, as well as in the size of the pores, the placement of the additive remaining fairly constant (Figure 4-b and 4-c). This process is accentuated in the CS3 sample, the additive being present on the whole surface of the sample.

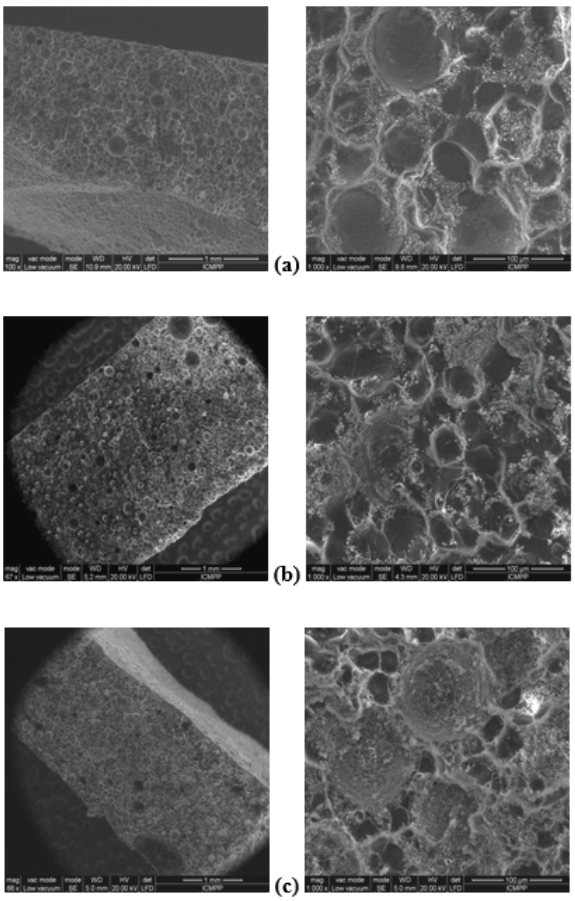

Fig. 2. SEM micrographs of samples: (a) CC1, (b) CC2, (c) CC3

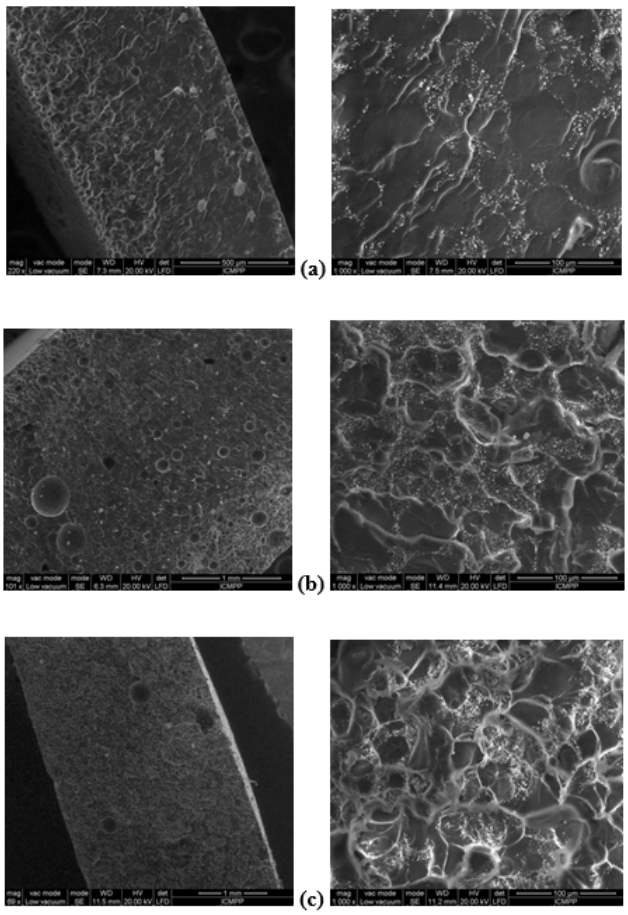

Fig. 3. SEM micrographs of samples: (a) CP1, (b) CP2, (c) CP3.

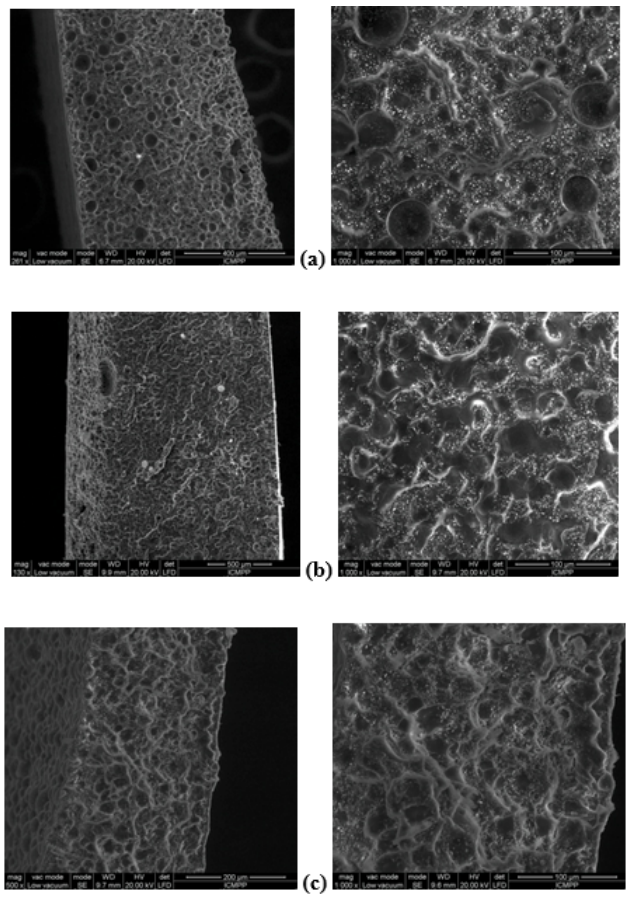

Fig. 4. SEM micrographs of samples:: (a) CS1, (b) CS2, (3) CS3

Conclusions

In the case of medical cements, the surface characteristics are of great importance because the gap represents the interface between the prosthesis and the bone.

The cement's high porosity, especially the one due to large size pores, is responsible for initiating and spreading cracks. The pores formed during the blending and introducing the material in the medullar channel allow the inclusion of air and as a result, the layer of cement loses resistance.

In order to obtain a stable fixation, all measures have to be taken to minimize both the size and number of the pores, because they can compromise a large number of cohesive bounds from the layer of cement.

The macroscopic properties of the cement can be modified substantially by varying the nature and/or component ratio: monomers, polymeric matrix.

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